



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Manganese-catalyzed Hydrofunctionalization of Alkenes

Citation for published version:

Thomas, S, Carney, J, Campbell, L & Dillon, B 2018, 'Manganese-catalyzed Hydrofunctionalization of Alkenes', *Angewandte Chemie International Edition*. <https://doi.org/10.1002/anie.201805483>

Digital Object Identifier (DOI):

[10.1002/anie.201805483](https://doi.org/10.1002/anie.201805483)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Angewandte Chemie International Edition

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



Manganese-catalyzed Hydrofunctionalization of Alkenes

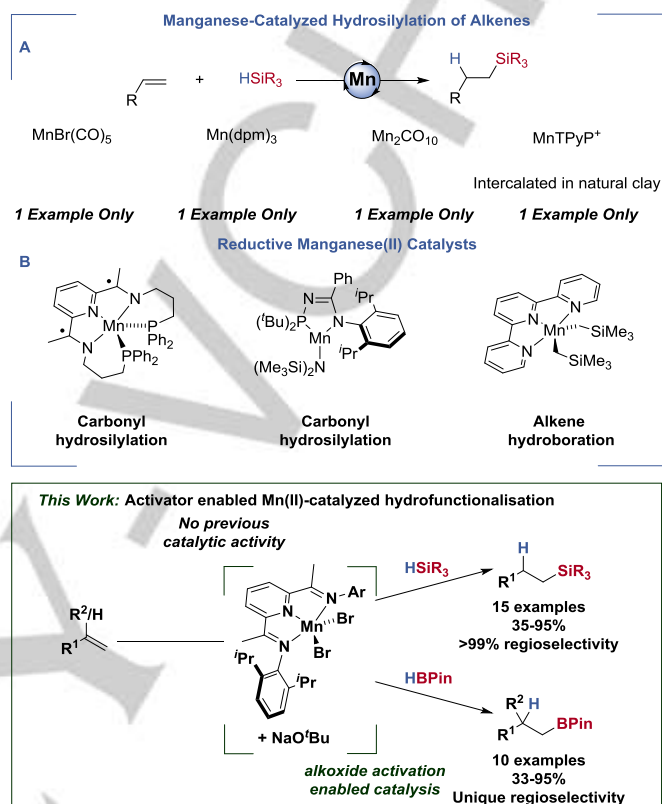
Jonathan R. Carney^[a], Barry R. Dillon^[b], Leonie Campbell^[b] and Stephen P. Thomas^{*,[a]}

Abstract: The manganese-catalyzed hydrosilylation and hydroboration of alkenes has been developed using a single Mn(II) pre-catalyst and reaction protocol. Both reactions proceed with excellent control of regioselectivity in high yields across a variety of sterically and electronically differentiated substrates (25 examples). Alkoxide activation, using NaO^tBu, was key to pre-catalyst activation and reactivity. Catalysis was achieved across various functional groups and on gram-scale across both the developed methodologies with catalysts loadings as low as 0.5 mol%.

The sustainable future of chemistry relies on the most efficient and strategic use of the Earth's critical resources and a greater application of abundant elements in the manufacture of ubiquitous materials, particularly those which are difficult to recycle. First-row transition metals are an obvious candidate for this, particularly for healthcare applications and large-scale disperse technologies. Despite being the third most abundant transition metal, manganese has not undergone the same resurgence in interest as other first-row transition metals.¹⁻³ For instance, the hydrosilylation of olefins has been reported with a range of iron and cobalt compounds but reports of manganese-catalysed equivalents are sporadic, and no example demonstrates the applicability of a catalyst to more than a single substrate.⁴⁻⁸

Olefin hydrosilylation is a \$15 billion per year industry which generates a wide-range of products with ubiquitous applications such as in soft plastics, weatherproofing and detergents.⁹⁻¹² Hydrosilylation reactions typically use a precious metal catalyst (most commonly a platinum species),¹³ but the scarcity, toxicity and cost of these metals mean they are not optimal for bulk chemical transformations.^{12,14} This is particularly the case for dispersive technologies with the hydrosilylation industry consuming roughly 5.6 billion tonnes of platinum per year.¹² Although iron and cobalt alternatives have been developed the substrate scope and ease of handling of these systems have yet to supplant the entrenched platinum complexes.

The manganese-catalysed hydrosilylation of polar double bonds such as aldehydes and ketones is well established.¹⁵⁻²² Examples also exist for the hydrosilylation of esters,^{21,23} amides²¹ and carboxylic acids²⁴ (Scheme 1, A). Recently, Wang and co-workers reported the first manganese-catalysed hydrosilylation of alkynes.²⁵ Despite these examples, the manganese-catalysed hydrosilylation of alkenes remains elusive; 4 singular examples have been published but they are severely limited in terms of optimisation, substrate scope and mechanistic work.⁴⁻⁸



Scheme 1. A) Manganese hydrosilylation catalysts. B) Mn(II) catalysts used in the hydrosilylation of carbonyls and hydroboration of alkenes. This work: the hydrofunctionalisation of alkenes using a Mn(II) pre-catalyst. dpm = tris(dipivaloyl)methanato; TPyP⁺ = tetra(4-pyridyl)porphyrin.

Iron and cobalt bis(imino)pyridine complexes are proficient catalysts for a wide range of reactions including: hydrogenation,²⁶ hydrosilylation²⁷ and hydroboration²⁷ amongst others.²⁸ Although manganese(II) bis(imino)pyridine compounds have been prepared²⁹ there are very limited reports of these operating as catalysts (Scheme 1, B).^{20,30} This inactivity has been ascribed to the behaviour of the high-spin Mn^{II} (S = 5/2) state.³¹ Recently Trovitch and co-workers reported the hydrosilylation of aldehydes, ketones and formates using a manganese(bis)imino pyridine species which was stabilized by pendant phosphine groups. This reduction proceeded with the highest TOF of any first-row transition metal catalyst for the hydrosilylation of ketones, demonstrating the potential of manganese catalysis for this type of transformation.^{23,32}

Having recently introduced the broad-range alkoxide activation of 1st-row transition metal pre-catalysts,^{7,33,34} we were keen to explore the possibilities of this method for reductive manganese(II) catalysis. We began this work by preparing a range of manganese(II) complexes, bearing tridentate amine ligands which have been widely used with other first-row transition metals in a range of catalysis (Table 1). Terpyridine manganese

[a] J. R. Carney, Dr S. P. Thomas
EaStCHEM School of Chemistry, University of Edinburgh,
Joseph Black Building, David Brewster Road, Edinburgh, EH9 3FJ,
UK.
E-mail: stephen.thomas@ed.ac.uk

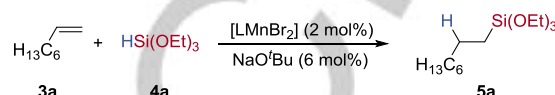
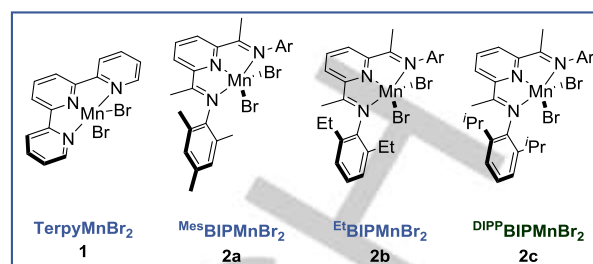
[b] B. R. Dillon, L. Campbell,
AstraZeneca,
Alderley Park, Macclesfield, Cheshire, SK10 4TG, UK

Supporting information for this article is given via a link at the end of the document.

COMMUNICATION

dibromide gave no catalytic activity (Table 1, Entry 1). An initial hit was found with the bis(imino)pyridine complex MesBIPMnBr_2 as the catalyst (Entry 2). Using 2 mol% of EtBIPMnBr_2 , 6 mol% NaO^tBu as the activator and triethoxysilane^{34,35} gave the hydrosilylation product in 90% yield with a regioselectivity of >99:1 linear:branched (Entry 3). Altering the *N*-aryl groups of the bis(imino)pyridine ligand showed that greater steric bulk led to increased catalytic activity, with 2,6-diisopropyl aniline-substituents giving the best result (Entry 4). Control reactions were carried out to demonstrate that both the manganese catalyst and NaO^tBu were required for successful catalysis (Entries 5–8). Alternative activators were also investigated, with other alkoxide salts giving comparable reactivity to NaO^tBu (Entries 9 and 10). Organometallic reagents, which have been extensively used for the *in situ* reduction of Fe(II) and Co(II) bis(imino)pyridine pre-catalysts such as EtMgBr ,^{36,37} NaBHET_3 ,^{38–42} LiAlH_4 ,^{43,44} and $\text{LiCH}_2\text{C}(\text{SiMe}_3)_3$ ⁴⁵ did not lead to any observed hydrosilylation products or catalyst activity (Entries 11–14).

The substrate scope of this system was explored using DIPPBIPMnBr_2 as the catalyst (2 mol%) and NaO^tBu (6 mol%) (Scheme 2). Octene hydrosilylation with industrially relevant silanes $\text{HSi}(\text{OEt})_3$, $\text{HSiMe}(\text{OEt})_2$ and primary silane PhSiH_3 all proceeded in excellent yields and regioselectivity to give the linear silanes, **5a–c**, respectively. Simple aliphatic alkenes **5d–f** underwent successful hydrosilylation in high yields and all aliphatic alkenes gave complete control of regioselectivity (>99:1) for the linear hydrosilylation product (**5a–l**). Complete chemoselectivity was also observed for a terminal alkene over an internal alkene **5g**. Alkene hydrosilylation in the presence of a cyclic tertiary amine, morpholine **5h** proceeded in high yield. Aryl groups with electron-withdrawing substituents such as a trifluoromethyl **5i**, fluoride **5j** and chloride **5k** substituents were all tolerated in the procedure, but an aryl bromide **5l** gave reduced hydrosilylation yields although no protodebromination was observed.⁴¹ Alkenes bearing pendant carbonyl groups **5l** underwent hydrosilylation, but only with excess silane and concurrent C=O bond reduction suggesting the rate of alkene hydrosilylation is slower than that of carbonyl hydrosilylation. Styrene derivatives **5n–5p** also underwent hydrosilylation although yields were significantly lower than that of the aliphatic alkenes (27–39%). The regioselectivity was also reduced with between 6% and 20% of the branched product being observed in these cases. The hydrosilylation product of 1-octene and $\text{HSi}(\text{OEt})_3$ **5a** used in commercial weatherproofing and cosmetic products.^{46,47} Thus to demonstrate the applicability of this methodology the hydrosilylation of 1-octene with $\text{HSi}(\text{OEt})_3$ was carried out on gram-scale using just 0.5 mol% of the manganese pre-catalyst to give 2.3 grams of the linear silane in a 95% isolated yield (Scheme 3) with only the linear regioisomer observed.



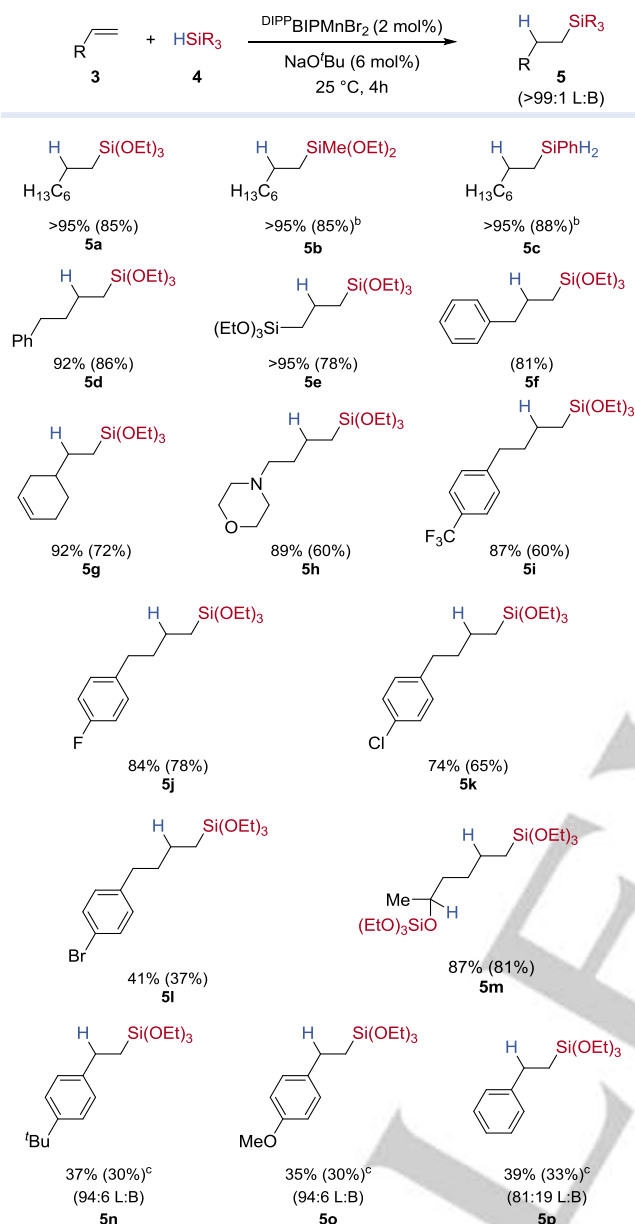
Entry	Catalyst	Reductant	Yield (%)
1	1	NaO^tBu	N.R.
2	2a	NaO^tBu	3
3	2b	NaO^tBu	90
4	2c	NaO^tBu	>95
5	MnBr_2	NaO^tBu	N.R.
6	2c	-	N.R.
7	DIPPBIP	-	N.R.
8	-	NaO^tBu	N.R.
9	2c	NaOMe	86
10	2c	KO^tBu	93
11	2c	EtMgBr	4
12	2c	NaBHET_3	trace
13	2c	LiAlH_4	N.R.
14	2c	$\text{LiCH}_2\text{C}(\text{SiMe}_3)_3$	N.R.

Reaction conditions: Alkene (0.5 mmol), HSiR_3 (0.63 mmol), catalyst (0.01 mmol), reductant (0.03 mmol), neat, 25 °C, 18 h. Yield determined by ^1H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Table 1. Screening of catalysts for the hydrosilylation of 1-octene.

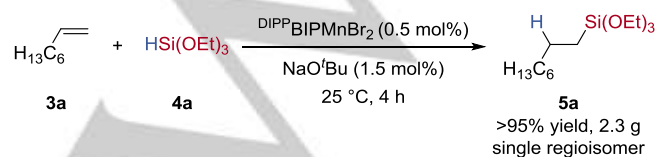
COMMUNICATION

Scheme 2: Hydrosilylation substrate scope



Reaction conditions: Alkene (1 mmol), HSiR_3 (1.25 mmol), $[\text{Mn}]$ (2 mol%), NaOtBu (6 mol%), neat, 25 °C, 4 h. Yield determined by ^1H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. Isolated yields in parenthesis. Regioselectivity is reported in parentheses as a ratio of linear:branched isomers. ^a **1b** used as catalyst. ^b 3 eq. of silane used. ^c Reaction time 18 h.

Scheme 3. Gram-scale reaction.



As manganese(II)-catalysed reduction reactions are rare and the paramagnetic nature of manganese species inhibits direct observation, the mechanisms of manganese-catalysis are not as well understood as other first-row transition metals. We carried out a series of mechanistic experiments to gain insight into this reaction. The catalyst activation was proposed to proceed through the *in-situ* formation of a hydrosiliconate species by the addition of *tert*-butoxide to triethoxysilane.^{7,33,34} Alkoxy hydrosilicates have been shown to react in a manner comparable to other hydride reagents (e.g. NaHBET_3 , LiAlH_4).⁴⁸ Therefore it was hypothesised that a pentacoordinate alkoxyhydrosilicate species could act as a hydride source and transfer a hydride to the manganese(II) pre-catalyst.⁴¹ From the manganese(II) dihydride species, a reductive-elimination event could give a formally low-oxidation state active catalyst. Stoichiometric mixing of KOEt and $\text{HSi}(\text{OEt})_3$ led to the formation of two silicon species, $\text{HSi}(\text{OEt})_4^-$ and the disproportionation product $\text{Si}(\text{OEt})_4$.³⁵ Addition of pre-catalyst DIPPBIPMnBr_2 led to the consumption of the hydrosiliconate species.

Further investigations of the mechanism were carried out through a series of trapping and poisoning experiments (Scheme 4). Initially, a control quench-reaction was carried out by addition of aqueous HCl (2M) 10 minutes after the pre-catalysts activation (addition of the alkoxide to the $\text{Mn}(\text{II})$ pre-catalyst). This gave a baseline reactivity of 12% hydrosilylation (Scheme 4, Entry 2). Next the homogeneity of the active catalyst was confirmed by trapping with dibenzo[a,e]-cyclooctatetraene (DCT) (Entry 3).^{44,49} The addition of DCT at equal loading to the pre-catalyst at the start of the reaction led to inhibition of the reaction, so only 36% of the hydrosilylation product formed. In order to determine if the reaction proceeded by a radical pathway a radical trap was added to a standard catalytic reaction. Addition of stoichiometric quantities with respect to pre-catalyst, of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) resulted in no inhibition of catalysis (Entry 4). Superstoichiometric quantities of TEMPO did somewhat inhibit the activity of the catalyst (Entry 5), however no octene-TEMPO adduct was observed.⁵⁰ Therefore a radical pathway is presumed to be unlikely. The trityl cations has been shown to act as a hydride abstractor for organometallic compounds.^{51,52} If a Mn-H is on the catalytic cycle, the addition of trityl cation should inhibit catalysis. The addition of stoichiometric amounts, with respect to pre-catalyst, of trityl hexachloroantimonate after 10 minutes led to complete inhibition of the reaction (Entry 6), equal to the quench using aqueous acid (Entry 2). The addition of smaller quantities of trityl cation led to proportional decreases in reactivity (Entry 7 + 8). It should be noted that two potential hydride sources are present under reaction conditions; the *in-situ* generated siliconate species and a possible Mn-H species. However, the addition of trityl cation 10 minutes after the activation of the pre-catalyst should preclude hydride trapping from the siliconate species as this has been consumed in pre-catalyst activation. The presence of super-stoichiometric amounts of NaOtBu (with respect to catalyst) did not lead to an increased yield suggesting Mn-H abstraction and subsequent catalyst deactivation is occurring. Hydrosilylation of 1,1,2- d_3 -4-phenyl-1-butene (deuterated alkene) led to scrambling of the deuterium at the internal carbon (C2) of the alkene (Scheme 4B) suggesting reversible hydrometallation.⁵³

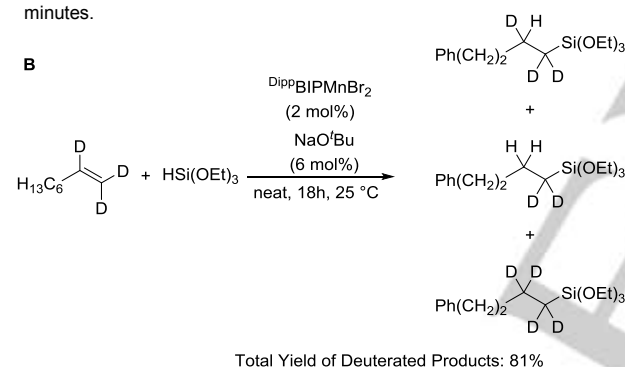
COMMUNICATION

Scheme 4: Mechanistic experiments

A

Entry	Additive	Mol %	Yield (%) ^a
1	-	-	>95
2	HCl (aq)	Excess	12 ^b
3		10	36
4		2	87
5		50	64
6	Ph	2	11 ^b
7	Ph	1	44 ^b
8	Ph	0.5	47 ^b

Reaction conditions: Octene (0.5 mmol), HSi(OEt)₃ (0.63 mmol), DIPPBIPMnBr₂ (0.01 mmol), NaO'Bu (0.03 mmol), neat, 25 °C, 18 h. ^a Yield determined by ¹H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. ^b additive added at 10 minutes.



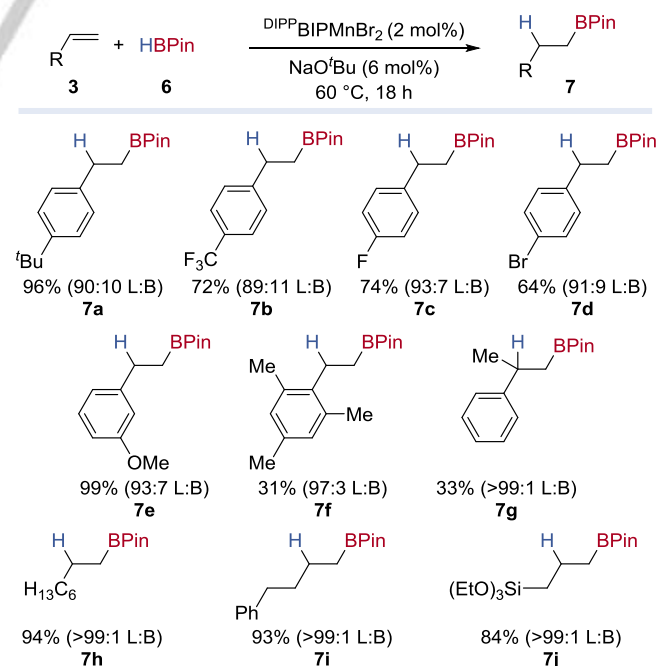
We postulated that the unique ability of NaO'Bu/DIPPBIPMnBr₂ for alkene hydrosilylation could potentially be expanded for broad use across other hydrofunctionalization reactions. For instance, the hydroboration of alkenes with pinacol borane gives stable and easily handled alkyl boronic ester products. Very recently, Fettinger and co-workers reported the hydroboration of alkenes using a dialkyl manganese catalyst bearing a terpyridine ligand to give boronic esters in high yields.⁵⁴ We postulated that replacement of the silane by pinacol borane in our system would facilitate a catalytically analogous reaction.

After minor optimization we found that replacing triethoxysilane with pinacolborane (3 equivalents) and increasing the reaction temperature to 60 °C allowed hydroboration to proceed in an otherwise identical system to that of the hydrosilylation. Styrenes bearing a range of sterically and electronically differentiated substituents all underwent successfully hydroboration in moderate to excellent yields (Scheme 5). Notably, the system gave excellent regiocontrol for the linear hydroboration product, in contrast to the single previous report of manganese-catalyzed hydroboration which selectively

gave the branched product for styrene derivatives.⁵⁴ 4-*tert*-Butylstyrene **7a** was hydroborated in high yield (96%) and regioselectivity (90:10 L:B). Strongly electron-withdrawing substituents such as a trifluoromethyl group **7b**, fluoride **7c** and bromide **7d** led to reduced reactivity (64–74%), although regioselectivity remained high (11–7% of the branched product observed). The presence of an electron-donating methoxy substituent gave high yields and improved regioselectivity **7e** (99%, 93:7 L:B). Using the heavily substituted 2,4,6-trimethylstyrene **7f** the hydroboration product was isolated with a reduced yield of 31% but with excellent control of regioselectivity. 1,1-Disubstituted styrenes were previously unreactive in manganese-catalyzed hydroboration.⁵⁴ However using the manganese-NaO'Bu conditions, α -methyl styrene gave the (racemic) linear boronic ester **7g**, albeit in a modest 33% isolated yield. Aliphatic alkenes such as 1-octene, 4-phenylbutene and 3-triethoxypropene underwent hydroboration in high yields with excellent control of regioselectivity **7h–j** (>99:1 L:B) exceeding those previously reported.⁵⁴

In summary, we have developed the manganese catalysed hydrosilylation and hydroboration of alkenes using a single manganese pre-catalyst which proceeds with high yield and excellent control of regioselectivity across both reactions. A bench-stable Mn(II) pre-catalyst and alkoxide activation with NaO'Bu were found to be uniquely active in addition to assisting operational simplicity. Successful catalysis was demonstrated across 25 substrates bearing a variety of functional groups and on gram-scale with catalyst loadings as low as 0.5 mol%. The operational simplicity of both transformations should allow exploitation and development by the wider community. The development of further manganese-catalysed reductive methodologies and mechanistic investigations are on-going and will be reported in due course.

Scheme 5: Hydroboration substrate scope



Reaction conditions: Alkene (1 mmol), HBPin (3 mmol), [Mn] (2 mol%), NaO^tBu (6 mol%), neat, 60 °C, 18 h. Isolated yields. Regioselectivities are reported below the yield in parentheses as a ratio of linear:branched isomers.

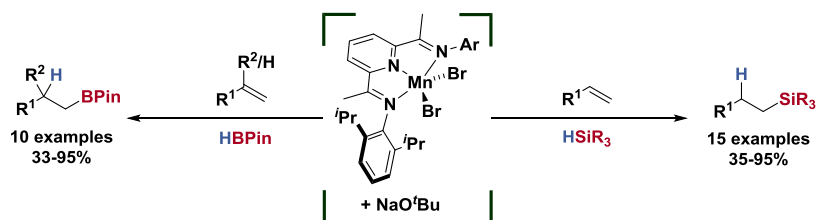
S.P.T. acknowledges the Royal Society for a University Research Fellowship. J.R.C. and S.P.T. acknowledge AstraZeneca for a PhD studentship.

Acknowledgements

Keywords: manganese • catalysis • hydrosilylation • alkenes • hydroboration

- (1) Carney, J. R.; Dillon, B. R.; Thomas, S. P. *Eur. J. Org. Chem* **2016**, 2016, 3912.
- (2) Valyaev, D. A.; Lavigne, G.; Lugan, N. *Coord. Chem. Rev.* **2016**, 308, Part 2, 191.
- (3) Garbe, M.; Junge, K.; Beller, M. *Eur. J. Org. Chem* **2017**, 2017, 4344.
- (4) Hilal, H. S.; Abu-Eid, M.; Al-Subu, M.; Khalaf, S. *J. Mol. Catal.* **1987**, 39, 1.
- (5) Pratt, S. L.; Faltynek, R. A. *J. Organomet. Chem.* **1983**, 258, C5.
- (6) Obradors, C.; Martinez, R. M.; Shenvi, R. A. *J. Am. Chem. Soc.* **2016**, 138, 4962.
- (7) Docherty, J. H.; Peng, J.; Dominey, A. P.; Thomas, S. P. *Nat Chem* **2017**, 9, 595.
- (8) Jondi, W.; Zyoud, A.; Mansour, W.; Hussein, A. Q.; Hilal, H. S. *Reaction Chemistry & Engineering* **2016**, 1, 194.
- (9) Abdellah, L.; Boutevin, B.; Youssef, B. *Prog. Org. Coat.* **1994**, 23, 201.
- (10) Harris, D. T.; STEWART, I. C.; GEORJON, O. J. F.; Blok, E. J.; Google Patents: 2015.
- (11) Sadlowski, E. S.; Soper, S. J.; Google Patents: 2013.
- (12) Holwell, A. J. *Platinum Metals Review* **2008**, 52, 243.
- (13) Troegel, D.; Stohrer, J. *Coord. Chem. Rev.* **2011**, 255, 1440.
- (14) Egorova, K. S.; Ananikov, V. P. *Angew. Chem. Int. Ed.* **2016**, 55, 12150.
- (15) Gregg, B. T.; Hanna, P. K.; Crawford, E. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1991**, 113, 384.
- (16) DiBiase Cavanaugh, M.; Gregg, B. T.; Cutler, A. R. *Organomet.* **1996**, 15, 2764.
- (17) Chidara, V. K.; Du, G. *Organomet.* **2013**, 32, 5034.
- (18) Son, S. U.; Paik, S.-J.; Lee, I. S.; Lee, Y.-A.; Chung, Y. K.; Seok, W. K.; Lee, H. N. *Organomet.* **1999**, 18, 4114.
- (19) Zheng, J.; Elangovan, S.; Valyaev, D. A.; Brousses, R.; César, V.; Sortais, J.-B.; Darcel, C.; Lugan, N.; Lavigne, G. *Adv. Synth. Cat* **2014**, 356, 1093.
- (20) Mukhopadhyay, T. K.; Flores, M.; Groy, T. L.; Trovitch, R. J. *J. Am. Chem. Soc.* **2014**, 136, 882.
- (21) Kelly, C. M.; McDonald, R.; Sydora, O. L.; Stradiotto, M.; Turculet, L. *Angew. Chem. Int. Ed.* **2017**, 56, 15901.
- (22) Ma, X.; Zuo, Z.; Liu, G.; Huang, Z. *ACS Omega* **2017**, 2, 4688.
- (23) Trovitch, R. J. *Synlett* **2014**, 25, 1638.
- (24) Zheng, J.; Chevance, S.; Darcel, C.; Sortais, J.-B. *Chem. Commun.* **2013**, 49, 10010.
- (25) Yang, X.; Wang, C. *Angew. Chem. Int. Ed.* **2018**, 57, 923.
- (26) Le Bailly, B. A. F.; Thomas, S. P. *RSC Adv.* **2011**, 1, 1435.
- (27) Greenhalgh, M. D.; Jones, A. S.; Thomas, S. P. *ChemCatChem* **2015**, 7, 190.
- (28) Flisak, Z.; Sun, W.-H. *ACS Catal.* **2015**, 5, 4713.
- (29) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, 107, 1745.
- (30) Britovsek, G. J. P.; England, J.; Spitzmesser, S. K.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2005**, 945.
- (31) Russell, S. K.; Bowman, A. C.; Lobkovsky, E.; Wieghardt, K.; Chirik, P. J. *Eur. J. Inorg. Chem.* **2012**, 2012, 535.
- (32) Trovitch, R. J. *Acc. Chem. Res.* **2017**, 50, 2842.
- (33) Peng, J.; Docherty, J. H.; Dominey, A. P.; Thomas, S. P. *Chem. Commun.* **2017**, 53, 4726.
- (34) Buslov, I.; Keller, S. C.; Hu, X. *Org. Lett.* **2016**, 18, 1928.
- (35) Buchwald, S. L. *Chem. Eng. News* **2**, 71, 2.
- (36) Greenhalgh, M. D.; Thomas, S. P. *Chem. Commun.* **2013**, 49, 11230.
- (37) Greenhalgh, M. D.; Frank, D. J.; Thomas, S. P. *Adv. Synth. Cat* **2014**, 356, 584.
- (38) Zhang, L.; Peng, D.; Leng, X.; Huang, Z. *Angew. Chem. Int. Ed.* **2013**, 52, 3676.
- (39) Peng, D.; Zhang, Y.; Du, X.; Zhang, L.; Leng, X.; Walter, M. D.; Huang, Z. *J. Am. Chem. Soc.* **2013**, 135, 19154.
- (40) Jia, X.; Huang, Z. *Nat Chem* **2016**, 8, 157.
- (41) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, 126, 13794.
- (42) Raya, B.; Biswas, S.; RajanBabu, T. V. *ACS Catal.* **2016**, 6, 6318.
- (43) Guo, N.; Hu, M.-Y.; Feng, Y.; Zhu, S.-F. *Org. Chem. Front.* **2015**, 2, 692.
- (44) Gieshoff, T. N.; Villa, M.; Welther, A.; Plois, M.; Chakraborty, U.; Wolf, R.; Jacobi von Wangelin, A. *Green. Chem.* **2015**, 17, 1408.
- (45) Sun, J.; Deng, L. *ACS Catal.* **2016**, 6, 290.
- (46) Curran, S.; Liao, K. S.; Alley, N.; Haldar, A.; Wang, A.; Google Patents: 2016.
- (47) Lorant, R.; GUILLIER, N.; Google Patents: 2013.
- (48) Corriu, R. J. P.; Guerin, C.; Henner, B.; Wang, Q. *Organomet.* **1991**, 10, 2297.
- (49) Anton, D. R.; Crabtree, R. H. *Organomet.* **1983**, 2, 855.
- (50) Albéniz, A. C.; Espinet, P.; López-Fernández, R.; Sen, A. J. *Am. Chem. Soc.* **2002**, 124, 11278.
- (51) Bahr, S. R.; Boudjouk, P. J. *Org. Chem.* **1992**, 57, 5545.
- (52) Straus, D. A.; Zhang, C.; Tilley, T. D. *J. Organomet. Chem.* **1989**, 369, C13.
- (53) See SI Page 45
- (54) Zhang, G.; Zeng, H.; Wu, J.; Yin, Z.; Zheng, S.; Fettingner, J. C. *Angew. Chem. Int. Ed.* **2016**, 55, 14369.

COMMUNICATION



Jonathan R. Carney, Barry R. Dillon,
Leonie Campbell and Stephen P.
Thomas*

Page No. – Page No.

**Manganese-Catalyzed
Hydrofunctionalization of Alkenes**

A single catalyst/activator platform is reported for the manganese-catalysed hydrosilylation and hydroboration of alkenes. The systems hinge on $NaOtBu$ operating as an activator and the reaction uses entirely bench-stable catalysts and reagents. Both reactions operate with high regioselectivity (up to >99:1) and in high yields (up to >95%).